LABORATORY CERTIFICATION AND REGISTRATION
WISCONSIN DEPT. OF NATURAL RESOURCES

LABNOTES Fall 1995

The Newsletter of the Wisconsin Laboratory Certification and Registration Program
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NR BOARD APPROVES PROPOSED RULE AMENDMENTS

The Natural Resources Board approved Order TS-22-95, revisions to Chs. NR 149, 219 and 700, Wis. Adm. Code on September 28, 1995. These revisions have been forwarded to the legislature for review and promulgation. The Board approved a slightly modified version of the proposed rules contained in the final Green Sheet package. The proposed language that was sent to the legislature contains two additional clarifications. First, a note which follows s. NR 149.15 was added to SECTION 22, regarding reporting data down to the limit of detection. The note reads:

Note: The requirement in sub. (3) becomes effective January 1, 1997 only for those substances with standards specified in chs. NR 105, 140 and 720 that are below the applicable limits of quantitation. Chapter NR 809 requires that this information be reported for all regulated drinking water contaminants. The department will annually publish a list of these substances. Laboratories should use the best available analytical science to determine whether, in their best professional judgement, a substance has been detected.

The Natural Resources Board also approved language that would require the program to obtain Board approval on fee adjustments using the proposed formula (SECTION 9, NR 149.05(1)(b)). The final proposed language reads:

(b) The total fee income shall be designed to generate revenues equal to the department of administration's approved spending authority for this program. The department may adjust the fee schedule according to the formulas in subds. 1 to 4 and the relative value items in table 2. Annual fee adjustments shall be reviewed by the laboratory certification standards review council and approved annually by the natural resources board.

Other significant items in the proposed rule package includes:

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PROPOSED RULE AMENDMENTS

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• A new test category structure affecting categories 11, 12 and 14. Categories 11 and 12 twelve will be divided between two new categories- Semivolatiles by GC and Semivolatiles by GC/MS. Category 14 will be revised to include all base/neutral extractable pesticides. These changes are intended to simplify certification categories and ease confusion pertaining to reference samples.

• Safe drinking water (SDWA) labs are required to notify regulated facilities of an MCL exceedance within 48 hours of analyzing a compliance sample.

• Beginning January 1, 1997, laboratories will be required to report all data greater than the limit of detection for those substances with standards below the limit of quantitation. Laboratories are expected to use professional judgement to determine whether a compound is detected.

• The EPA's SW-846 methods will be allowed for analyzing wastewater samples.

• The holding time prior to solvent addition for DRO is 72 hours for all samples. No weekend allowance will be given. This change was a result of public comments from laboratories and consultants. The Department has initiated a study to determine if the 72 hour holding time will affect sample integrity. The results of this research will be published early in 1996.

• Methanol preservation is required for all soil samples collected for volatile organics analysis.

• The September 1995 DRO and GRO are incorporated by reference into chapters NR 149 and 700. These methods are modifications of the 1993 methods.

We expect these revisions to become effective in the spring of 1996. The Laboratory Certification Program will work closely with all affected labs in the coming months to insure a smooth transition into the new requirements. Informational meetings may be held across the state if laboratories express an interest in this type of forum for discussion of the changes. Laboratories can expect to receive a category selection and certification update form in the mail soon after the rules are promulgated. The proposed rules are available for free downloading on the DNR's internet gopher. (See article, page 7). Contact Jeff Ripp at (608) 267-0579 or Jack Sullivan at (608) 267-9753 for more information regarding the rule changes.

LAB CERT PROGRAM PREPARES FOR AG PESTICIDES CERTIFICATION

To accommodate the surging interest in performing analytical work associated with agricultural pesticide spills and misuse clean-ups, the Laboratory Certification Program is gearing up to certify and audit interested laboratories. Lab Cert staff have met with representatives of the Department of Agriculture, Trade, and Consumer Protection and have agreed to certify laboratories for pesticide methods currently available in the authoritative sources, and for the analytes contained therein.

Although this will allow certification for most of the pesticides commonly used in Wisconsin, methods are still not available or have not been validated for many pesticides, especially in soil. Because the Ground Water Quality (NR 140) rule establishes a standard for atrazine and its common metabolites, We are investigating modifications necessary to analyze the metabolites using currently approved methods.

LAB CERT PROGRAM PREPARES FOR AG PESTICIDES CERTIFICATION

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Responding to public comments made during the latest round of revisions to the Lab Cert Code, NR 149 will now collect all base/neutral and acid extractable pesticides under one test category. This test category will cover organophosphorus pesticides, atrazine and its metabolites, and other nitrogen containing pesticides. The two other existing test categories that include pesticides are category 13, which contains pesticides analyzable by liquid chromatography, and category 16, which contains organochlorine pesticides. Contact Alfredo Sotomayor at (608) 266-9257 for more information about pesticide certification.

WHERE HAS ALL THE FREON GONE

We have heard that freon shipments are disappearing in transit. When labs can get freon-113, it comes with a premium price. Various labs have asked when they will be able to use the replacement method for oil and grease. Unfortunately, EPA has not officially proposed method 1664 (HEM), the n-hexane alternative. Although initial comparisons suggested a lack of statistical agreement between the two methods, subsequent studies have led EPA to conclude that HEM results were within the method error of the freon extraction. Rumor has it that the method was revised in January 1995, the proposed changes are waiting for final sign-off, and EPA anticipates proposing it in the Federal Register in the near future.

In anticipation of the freon extraction's ultimate demise, we included method 1664 in the amendments to Ch. NR 219 currently undergoing legislative review. Copies of this method, "Method 1664: n-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry should be available from the EPA Water Resources Center (202)260-7786. If you intend to continue testing for oil and grease and haven't begun method development yet, we recommend that you start now. We understand that labs will be allowed to use solid phase extraction if method performance criteria are met.

Laboratory certification will cover this procedure in the test category 4, Physical; however Method 1664 will be identified as HEM or SGT-HEM, not as oil and grease. Until December 31, 1995, labs can request certification for method 1664 by sending us a letter with their initial demonstration of capability (IDC) and method detector limit (MDL) determination. If requested in 1996, we will ask for a revised application with the appropriate fee. See the related article on Standard Format for MDL and IDC Submittals.

The Wastewater Program is exploring mechanisms to allow use of Method 1664 in advance of final EPA action. They are also considering ways to effectively communicate the details to everyone affected. For pretreatment monitoring, municipal ordinances may be a controlling factor. In the transition period, we believe that it is important to clearly identify which method was used to generate compliance results. Facilities with compliance problems for oil and grease may want to monitor using both methods to establish a source-specific comparison. Contact John Condron at (608) 267-2300 or Donalea Dinsmore at (608) 266-8948 for more information.

PRESERVATION OF NITRATE AND TOTAL NITRATE/NITRITE IN DRINKING WATER SAMPLES.

Recently, there has been some confusion regarding the preservation requirements of nitrate and total nitrate/nitrite in drinking water samples. The auditors in the Laboratory Certification Program have just received written clarification of the requirements from the EPA at Region 5. If samples to be analyzed for nitrate are cooled to 4° C at the time of collection and analyzed within 48 hours, no further preservation is needed. If nitrate samples cannot be analyzed within 48 hours, preservation with sulfuric acid to pH < 2 at the time of collection and analysis within 14 days is allowed. However, once sulfuric acid is added, the value obtained is "total" nitrate unless previous knowledge of the sample shows that no nitrite is present. In addition, when samples to be analyzed for total nitrate plus nitrite are cooled to 4° C at the time of collection and analyzed within 48 hours,then sulfuric acid preservation can be omitted. For more information, contact Deb Piper at (608) 264-8950.

REFERENCE SAMPLE PROVIDERS EXPAND SERVICE, WI INCLUDES ASI

NEW! **-** The Laboratory Certification Program is happy to announce the conditional approval of Analytical Standards Inc. (ASI) as an acceptable reference sample provider effective July 1, 1995. ASI provides double-blind reference samples several times throughout the year. Studies dated later than July 1, 1995 will be acceptable for renewal provided they meet the minimum criteria established for the other providers. Contact ASI at 1800-AUDIT-44 or Rick Mealy at (608) 264-6006 for more information.

NEW TOO! **-** Lab Cert has worked out an agreement with ERA regarding their Quick Reference™ program. Beginning January 1, 1996 the Laboratory Certification Program will accept Quick Reference™ samples for applications, renewals and corrective actions for most parameters. The Quick Reference samples cannot be used for category 18- Safe Drinking Water. Since ERA will soon be submitting this data to the Department electronically on 3.5" diskettes, it is important to inform ERA that the results will be used for Wisconsin compliance when ordering samples. Contact ERA at 1-800-ERA-0122 to order samples or Rick Mealy at (608) 264-6006 for more information.

REFERENCE SAMPLE REMINDERS

It is generally a good idea to maintain a subscription to one of the approved providers. This will insure that you always receive the samples you need on time for renewal. Many providers are willing to provide electronic data submittal to Wisconsin. We encourage labs to use this service, as it cuts down data entry errors and saves time.

- Base Neutral Extractables - Not all providers are able to meet the criteria for a "representative sample". In order to be considered representative, a reference sample for semivolatiles by GC/MS (method 8270) should contain between 15 - 30 base/neutral and acid extractable compounds. Also, to be representative for B/N extractables the sample needs to contain at least one analyte from four the following: phthalate esters, PAHs, haloethers, nitrosamines, nitroaromatics nonpurgeable chlorinated hydrocarbons and isophorone. (Continued on p. 5)

BASE NEUTRAL EXTRACTABLES

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Currently, the EPA-WS and EPA-WP studies are not acceptable for semivolatiles by GC/MS. Acceptable samples are available from the State Lab of Hygiene, ERA, APG and the New York Department of Health.

- Petroleum Hydrocarbons -

The only acceptable provider of reference samples for GRO, DRO and PVOCs continues to be the Wisconsin State Laboratory of Hygiene. Samples may be ordered by calling (608) 833-1770, extension 108.

- SDWA -

The only acceptable provider of reference samples for the regulated drinking water parameters continues to be the EPA-WS study. We are exploring the possibility of allowing other providers for corrective action situations.

DNR NEWS BRIEFS

★ The legislature approved Order WR-19-94, revisions to Chs. NR 140 and 149, Wis. Adm. Code. These revisions became effective on September 1, 1995. Included in these revisions were several minor modifications to Ch. NR 149, the Laboratory Certification code. The revisions amend the definitions of LOD and LOQ for consistency with Ch. NR 140 and clarify the requirements for the use of method blanks. Copies of the revised code language are available from the Office of Technical Services or the DNR Gopher.

★ As you may know the Wisconsin Department of Natural Resources is in the process of reorganizing the agency. The planning portion of the reorganization should be completed by the end of the year and implementation begins in January 1996. The Office of Technical Services will be combined with other bureaus, and will reside in the new Division of Administration and Technology. We expect little or no interruption of services to our customers during the reorganization process. We will keep you posted on the status of the Laboratory Certification Program as the reorganization progresses.

★ Those of you who have been to Madison to review our files are aware of the limitations of our old filing system. We are currently in the process of arranging a new filing system which should make it easier and faster to find information and we anticipate completing the project by the first of the year. The new system will organize our files by FID number, and each audit, application, etc. will have a separate clearly labelled folder. The files are always open, and we encourage anybody interested in looking at the files to stop by. Arrangements for a visit can be made with Carol Lochner at (608) 267-7633.

AUDITOR'S CORNER

CALIBRATIONS--FOUR PRECEPTS AND AN ADMONITION

- Alfredo Sotomayor,
  Senior Audit Chemist

Calibration is traditionally a procedure for adjusting, tuning, or verifying the accuracy of an instrument exactly. In this sense, a chemist calibrates a pipet, a balance, a buret, or a thermometer. However, in another sense, we calibrate to **establish** a relationship between instrument response and concentration of analyte. We accomplish the latter by constructing a calibration curve.

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AUDITOR'S CORNER
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Many of the most common deficiencies we find during audits involve improper calibrations. When once asked to confess what I would spend time reviewing in a large laboratory where I only had a few hours to perform an audit, I answered that I would focus on calibrations. No amount of corroboratory QC can save an improperly calibrated system.

• **Keep it simple: go linear.**

The majority of the instruments used in the environmental laboratory relate response to concentration linearly, or transform the primary signal to produce a linear output. Although deviations from linearity are encountered in the analytical range, they are more common at the extremes, where detector saturation or insensitivity are the culprits. The simplest way of obtaining a calibration curve is to use linear regression, and the most defensible way to do this pairs concentration and response to the x and y coordinates, respectively.

• **Know when to include a zero.**

Unless you are using a calibration algorithm that fits points exactly, you will have to decide what to do about blank signals. I follow this rule of thumb: if I can adjust my instrument to read zero in the presence of a blank, then I include a zero point in my calibration curve. Including a zero would be appropriate for spectrophotometers -- UV/VIS, AA, and ICP -- but would not be for chromatographs, or the mass spectrometer.

• **Do not <u>force</u> curves through zero.**

Doing this manipulates the data mathematically to obtain a y-intercept equal to zero. As a result, we lose valuable information about the lower limits of the analytical signal, and a good estimator of the limit of detection on the calibration day. Even when it is justified to include a zero point in the calibration curve, forcing the intercept to read zero is not.

• **Define your calibration range properly.**

You would not use a telescope to examine a cell, or a microscope to observe lunar craters. For low level work, it is best to choose points above but near detection limits. For high level work, defining the upper limit of the calibration range is more important. The most accurate results are obtained when the signals we find in unknowns are close to those found in the knowns used to establish the calibration curve. A good calibration curve is like a well- maintained highway: it has legible signs and evenly spaced markers. All curves should be accompanied by the equations or coefficients that define them and should be generated using, as much as possible, evenly distributed points, the more (at least three), the better.

And as an auditor, I leave you with the following admonition:

• Always use the full calibration curve to quantitate samples. Never use the daily calibration verification standard to quantitate unknowns.

REMINDERS!

☞ Please put your nine digit Facility Identification number (FID) on all correspondence with the Laboratory Certification Program. This insures proper filing and easy identification.

☞ The direct fax line for the Office of Technical Services is (608) 267-5321. Please use this line when sending transmittals pertaining to certification.

☞ According to ch. NR 219, Wis. Adm. Code, (wastewater compliance) all analyses for ammonia require distillation unless a comparability study has been

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REMINDERS!

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done and demonstrates there are no interferants present in the effluent. For wastewater effluent this study has been done for ion selective electrodes. You can request this study from our office. The study does not apply to other methods of analysis or to industrial effluents.

☞ If your instruments are equipped with capillary columns, reference and use methods written for capillary columns when they are available.

LABORATORY CERTIFICATION ON THE INTERNET

The Department of Natural Resources maintains a gopher accessible via the internet (URL gopher:\\dnrdns.dnr.state.wi.us). In addition to providing interesting information about the DNR, upcoming events, outdoor news, and the fishing reports, the gopher contains information pertaining to Biomonitoring Certification. We are in the process of developing a gopher for Laboratory Certification which will hopefully be in place within the next several months. Look for the Laboratory Certification program under the "Environmental Programs" directory. Access to the internet is essential for those wishing to use the gopher. Direct internet connections are available for a fee in many locations, and commercial services such as America Online provide internet access as part of their software packages. The Department is also investigating the possibility of maintaining a World Wide Web server. If this becomes reality, all DNR programs will have the opportunity to develop home pages. Contact Jeff Ripp by e-mail at rippj@dnr.state.wi.us or by calling (608) 267-0579 or for more information about accessing and using the gopher.

STANDARD DATA SUBMITTAL FORMS

The Laboratory Certification Program requests that all laboratories submitting MDLs and IDCs to the Department use something similar to the standard form below. This expedites data review and insures that we get all of the information we need. The submittal forms for MDLs and IDCs should contain the following information at a minimum:

MDL Format

Analyte/Matrix	Spike Concentration	Replicate #1 (ug/L, etc.)	#2	#3	#4	#5	#6	#7	Standard Deviation	Mean	MDL

IDC Format

Analyte/ Matrix	Spike Concentration	Replicate #1 (ug/L, etc.)	#2	#3	#4	#5 if required	Standard Deviation	Mean	Mean % Recovery	RSD

% Recovery	-------						------	------		------

NEW GRO, DRO METHODS AVAILABLE

• The September 1995 versions of the Wisconsin Modified GRO method (WI-PUBL-SW-140) and Wisconsin Modified DRO method (WI-PUBL-SW-141) have been approved by the Natural Resources Board and are being incorporated by reference into Chs. NR 149 and 700, Wis. Adm. Code. These documents are expected to be promulgated in early 1996. Copies of the proposed final methods (not yet approved by the legislature) are available electronically on the LUST electronic bulletin board and on the DNR Gopher. To access the bulletin board, dial (608) 261-6455 with your modem. To access the files through the gopher, go to the address dnrdns.dnr.state.wi.us and find the sep95dro.zip and sep95gro.zip files in the /environmental programs/laboratory certification/downloads directory. Hard copies of the documents are also available for a fee from Dawn Camacho, ERR Section, Department of Natural Resources, 101 S. Webster St., Madison, WI, 53707, phone (608) 261-6424, for a fee. Please send a check to cover the cost of printing and mailing. The price for the GRO method is $3.50, the DRO method is $2.50, and both methods together cost $6.00. We do not anticipate any further changes to the methods. However, after promulgation, the final approved methods will be announced in the "LUST Release News" and will be similarly available.

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